

We Claim:

1. A creped fibrous web wherein in the creping process the Yankee dryer surface is treated with a creping adhesive that comprises:
- a) an adhesive composition comprising organic polymers having in the polymer backbone amine groups selected from the group consisting of primary and secondary amines or mixtures of primary and secondary amines and a zirconium compound ^{1, 2} having a valence of plus four suitable for crosslinking by ionic crosslinking with cellulosic paper products,
 - No of a compound* b) in an amount sufficient to promote improvement in adhesion and to effect creping.
2. The creped fibrous web of Claim 1 wherein the organic polymer having primary and secondary amine groups is selected from the group consisting of chitosan, polyvinylamine, polyvinyl alcohol-vinyl amine and polyaminoamide.
3. The creped fibrous web of Claim 1 or 2 wherein the zirconium compound is selected from the group consisting of ammonium zirconium carbonate, zirconium acetylacetonate, zirconium acetate, zirconium carbonate, zirconium sulfate, zirconium phosphate, potassium zirconium carbonate, zirconium sodium phosphate and sodium zirconium tartrate.
4. The creped fibrous web of Claim 1 or 2 wherein the zirconium compound is ammonium zirconium carbonate.
5. The creped fibrous web of Claim 1 or 2 wherein about 0.1 to about 0.8 pounds of the adhesive formulation are added for each ton of cellulosic papermaking fibers in the aqueous furnish.

6. The creped fibrous web of Claim 1 or 2 wherein about 0.1 to about 10 pounds of the cationic softener/debinder are added for each ton of the cellulosic papermaking fibers in the aqueous furnish.

7. The creped fibrous web of Claim 6 wherein the nitrogenous softener/debinder is selected from the group consisting of imidazolines, amido amine salts, linear amido amines, tetravalent ammonium salts, and mixtures thereof.

8. The creped fibrous web of Claim 7 wherein the salt has the following structure:



wherein EDA is a diethylenetriamine residue, R is the residue of a fatty acid having from 12 to 22 carbon atoms, and X is an anion.

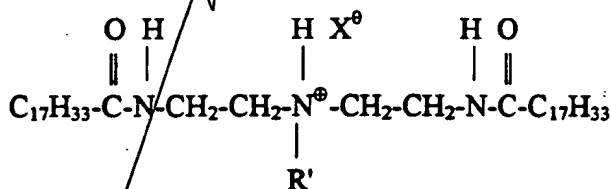
9. The creped fibrous web of Claim 6 wherein the salt has the following structure:



wherein R is the residue of a fatty acid having from 12 to 22 carbon atoms, R' is a lower alkyl group, and X is an anion.

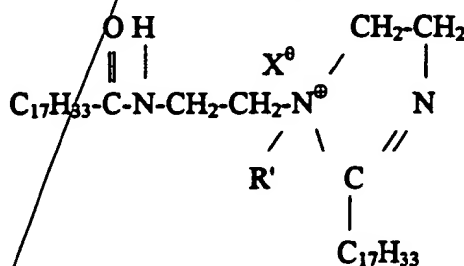
10. The creped fibrous web of Claim 6 wherein the softener/debinder is a mixture of linear amido amines and imidazolines of the following structure:

(i)



and

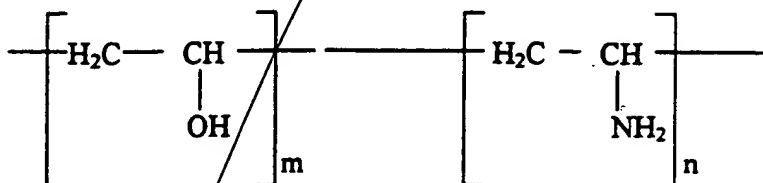
(ii)



wherein X is an anion.

11. A creped fibrous web where in the creping process the Yankee dryer surface is treated with a creping adhesive that comprises:

- a) an adhesive composition comprising polyvinyl alcohol-vinyl amine copolymer of the following structure:



wherein m and n have values of about 1 to 99 and about 99 to 1 respectively, and a zirconium crosslinking agent having a valence of plus four that can be crosslinked by ionic crosslinking with cellulosic paper products,

- b) in an amount sufficient to promote improvement in adhesion and effect the creping.

12. The creped fibrous web of Claim 11 wherein the zirconium compound is selected from the group consisting of ammonium zirconium carbonate, zirconium acetylacetonate, zirconium acetate, zirconium carbonate, zirconium sulfate, zirconium phosphate, potassium zirconium carbonate, zirconium sodium phosphate and sodium zirconium tartrate.

13. The creped fibrous web of Claim 11 wherein the zirconium compound is ammonium zirconium carbonate.

14. The creped fibrous web of Claim 11 wherein about 0.1 to about 0.8 pounds of the adhesive formulation are added for each ton of cellulosic papermaking fibers in the aqueous furnish.

15. The creped fibrous web of Claim 11 wherein about 0.1 to about 10 pounds of the cationic softener/debonder are added for each ton of the cellulosic papermaking fibers in the aqueous furnish.

16. The creped fibrous web of Claim 15 wherein the nitrogenous softener/debonder is selected from the group consisting of imidazolines, amido amine salts, linear amido amines, tetravalent ammonium salts, and mixtures thereof.

17. The creped fibrous web of Claim 16 wherein the salt has the following structure:



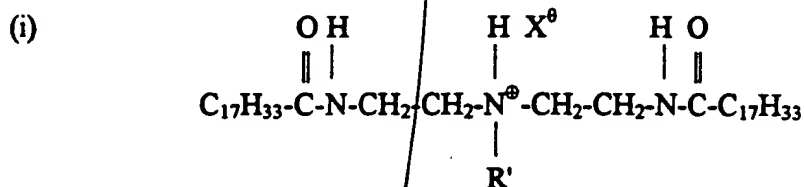
wherein EDA is a diethylenetriamine residue, R is the residue of a fatty acid having from 12 to 22 carbon atoms, and X is an anion.

18. The creped fibrous web of Claim 15 wherein the salt has the following structure:



wherein R is the residue of a fatty acid having from 12 to 22 carbon atoms, R' is a lower alkyl group, and X is an anion.

19. The creped fibrous web of Claim 15 wherein the softener/debonder is a mixture of linear amido amines and imidazolines of the following structure:



and

$$\begin{array}{c}
 \text{O} \quad \text{H} \\
 || \quad | \\
 \text{C}_{17}\text{H}_{33}-\text{C}-\text{N}-\text{CH}_2-\text{CH}_2-\text{N}^{\oplus} \\
 \diagdown \quad / \\
 \text{R}' \quad \text{X}^{\ominus}
 \end{array}
 \quad
 \begin{array}{c}
 \text{CH}_2-\text{CH}_2 \\
 | \qquad | \\
 \text{N} \qquad \text{C} \\
 // \qquad | \\
 \text{C}_{17}\text{H}_{33}
 \end{array}$$

20. A creped towel wherein in the creping process the Yankee dryer surface is treated with a creping adhesive that comprises:

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23. The creped towel of Claim 20 or Claim 21 wherein the zirconium compound is ammonium zirconium carbonate.

24. The creped towel of Claim 20 or Claim 21 wherein about 0.1 to about 0.8 pounds of the adhesive formulation are added for each ton of cellulosic papermaking fibers in the aqueous furnish.

25. The creped towel of Claim 20 or Claim 21 wherein about 0.1 to about 10 pounds of the cationic softener/debonder are added for each ton of the cellulosic papermaking fibers in the aqueous furnish.

26. The creped towel of Claim 25 wherein the nitrogenous softener/debonder is *anion* selected from the group consisting of imidazolines, amido amine salts, linear amido amines, tetravalent ammonium salts, and mixtures thereof.

27. The creped towel of Claim 26 wherein the salt has the following structure:



wherein EDA is a diethylenetriamine residue, R is the residue of a fatty acid having from 12 to 22 carbon atoms, and X is an anion.

28. The creped towel of Claim 25 wherein the salt has the following structure:



wherein R is the residue of a fatty acid having from 12 to 22 carbon atoms, R' is a lower alkyl group, and X is an anion.

29. The creped towel of Claim 25 wherein the softener/debonder is a mixture of linear amido amines and imidazolines of the following structure:

(i)

32. The creped towel of Claim 30 wherein the zirconium compound is ammonium zirconium carbonate.

33. The creped towel of Claim 30 wherein about 0.1 to about 0.8 pounds of the adhesive formulation are added for each ton of cellulosic papermaking fibers in the aqueous furnish.

34. The creped towel of Claim 30 wherein about 0.1 to about 10 pounds of the cationic softener/debonder are added for each ton of the cellulosic papermaking fibers in the aqueous furnish.

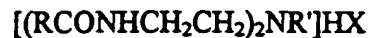
35. The creped towel of Claim 34 wherein the nitrogenous softener/debonder is selected from the group consisting of imidazolines, amido amine salts, linear amido amines, tetravalent ammonium salts, and mixtures thereof.

36. The creped towel of Claim 35 wherein the salt has the following structure:



wherein EDA is a diethylenetriamine residue, R is the residue of a fatty acid having from 12 to 22 carbon atoms, and X is an anion.

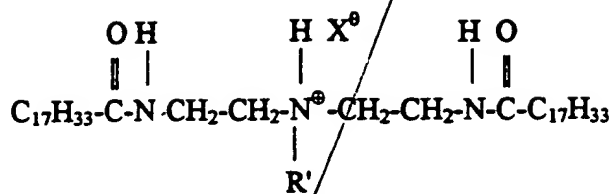
37. The creped towel of Claim 34 wherein the salt has the following structure:



wherein R is the residue of a fatty acid having from 12 to 22 carbon atoms, R' is a lower alkyl group, and X is an anion.

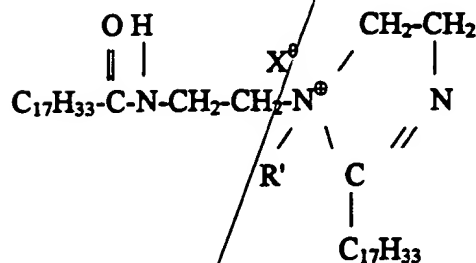
38. The creped towel of Claim 34 wherein the softener/debonder is a mixture of linear amido amines and imidazolines of the following structure:

(i)



and

(ii)



wherein X is an anion.

39. A creped tissue wherein in the creping process the Yankee dryer surface is treated with a creping adhesive that comprises:

- a) an adhesive composition comprising organic polymers having in the polymer backbone amine groups selected from the group consisting of primary and secondary amines or mixtures of primary and secondary amines and a zirconium compound having a valence of plus four suitable for crosslinking by ionic crosslinking with cellulosic paper products,
- b) in an amount sufficient to promote improvement in adhesion and to effect creping.

40. The creped tissue of Claim 39 wherein the organic polymer is selected from the group consisting of chitosan, polyvinylamine, polyvinyl alcohol-vinyl amine and polyaminoamide.

41. The creped tissue of Claim 39 or Claim 40 wherein the zirconium compound is selected from the group consisting of ammonium zirconium carbonate, zirconium acetylacetonate, zirconium acetate, zirconium carbonate, zirconium sulfate, zirconium phosphate, potassium zirconium carbonate, zirconium sodium phosphate and sodium zirconium tartrate.

42. The creped tissue of Claim 39 or Claim 40 wherein the zirconium compound is ammonium zirconium carbonate.

43. The creped tissue of Claim 39 or Claim 40 wherein about 0.1 to about 0.8 pounds of the adhesive formulation are added for each ton of cellulosic papermaking fibers in the aqueous furnish.

44. The creped tissue of Claim 39 or Claim 40 wherein about 0.1 to about 10 pounds of the cationic softener/debonder are added for each ton of the cellulosic papermaking fibers in the aqueous furnish.

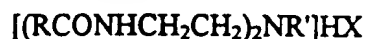
45. The creped tissue of Claim 44 wherein the nitrogenous softener/debonder is selected from the group consisting of imidazolines, amido amine salts, linear amido amines, tetravalent ammonium salts, and mixtures thereof.

46. The creped tissue of Claim 45 wherein the salt has the following structure:



wherein EDA is a diethylenetriamine residue, R is the residue of a fatty acid having from 12 to 22 carbon atoms, and X is an anion.

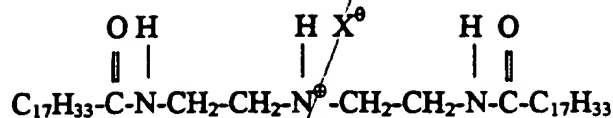
47. The creped tissue of Claim 44 wherein the salt has the following structure:



wherein R is the residue of a fatty acid having from 12 to 22 carbon atoms, R' is a lower alkyl group, and X is an anion.

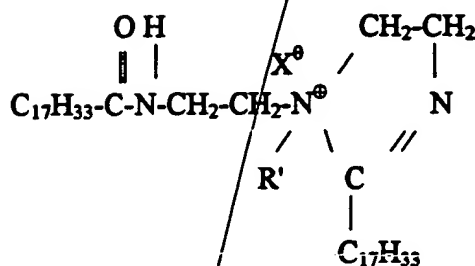
48. The creped tissue of Claim 44 wherein the softener/debonder is a mixture of linear amido amines and imidazolines of the following structure:

(i)



and

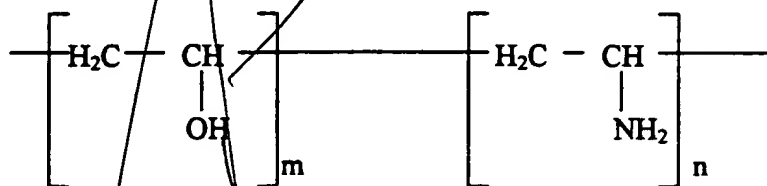
(ii)



wherein X is an anion.

49. A creped tissue where in the creping process the Yankee dryer surface is treated with a creping adhesive that comprises:

a) an adhesive composition comprising polyvinyl alcohol-vinyl amine copolymer of the following structure:



wherein m and n have values of about 1 to 99 and about 99 to 1 respectively, and a zirconium crosslinking agent having a valence of plus four that can be crosslinked by ionic crosslinking with cellulosic paper products,

b) in an amount sufficient to promote improvement in adhesion and effect the creping.

50. The creped tissue of Claim 49 wherein the zirconium compound is selected from the group consisting of ammonium zirconium carbonate, zirconium acetylacetonate, zirconium acetate, zirconium carbonate, zirconium sulfate, zirconium phosphate, potassium zirconium carbonate, zirconium sodium phosphate and sodium zirconium tartrate.

51. The creped tissue of Claim 49 wherein the zirconium compound is ammonium zirconium carbonate.

52. The creped tissue of Claim 49 wherein about 0.1 to about 0.8 pounds of the adhesive formulation are added for each ton of cellulosic papermaking fibers in the aqueous furnish.

53. The creped tissue of Claim 49 wherein about 0.1 to about 10 pounds of the cationic softener/debonder are added for each ton of the cellulosic papermaking fibers in the aqueous furnish.

54. The creped tissue of Claim 53 wherein the nitrogenous softener/debonder is selected from the group consisting of imidazolines, amido amine salts, linear amido amines, tetravalent ammonium salts, and mixtures thereof.

55. The creped tissue of Claim 54 wherein the salt has the following structure:



wherein EDA is a diethylenetriamine residue, R is the residue of a fatty acid having from 12 to 22 carbon atoms, and X is an anion.

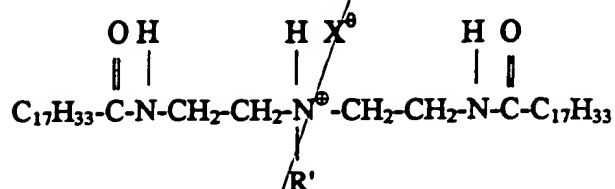
56. The creped tissue of Claim 53 wherein the salt has the following structure:



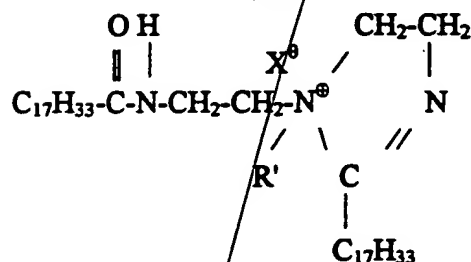
wherein R is the residue of a fatty acid having from 12 to 22 carbon atoms, R' is a lower alkyl group, and X is an anion.

57. The creped tissue of Claim 53 wherein the softener/debonder is a mixture of linear amido amines and imidazolines of the following structure:

(i)



(ii)



wherein X is an anion.

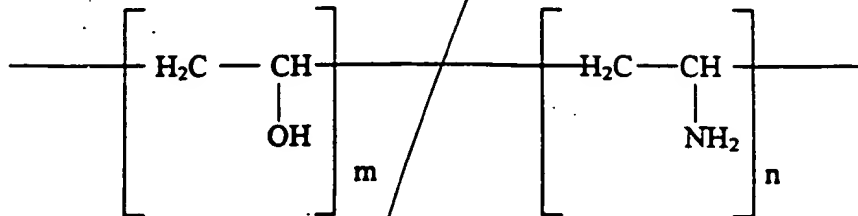
58. A creping adhesive composition comprising organic polymers having in the polymer backbone amine groups selected from the group consisting of primary and secondary amines or mixtures of primary and secondary amines and crosslinkable zirconium compounds having a valence of plus four suitable for crosslinking with cellulosic paper products wherein the polymer and zirconium compound are crosslinkable at the drying surface.

59. ^{creping} The adhesive composition of Claim 58 wherein the organic polymer is selected from the group consisting of chitosan, polyvinylamine, polyvinyl alcohol-vinyl amine and polyaminoamide.

60. The creping adhesive of Claim 58 or Claim 59 wherein the zirconium compound is selected from the group consisting of ammonium zirconium carbonate, zirconium acetylacetonate, zirconium acetate, zirconium carbonate, zirconium sulfate, zirconium phosphate, potassium zirconium carbonate, zirconium sodium phosphate and sodium zirconium tartrate.

61. The creping adhesive of Claim 58 or Claim 59 wherein the zirconium compound is ammonium zirconium carbonate.

62. A creping adhesive composition comprising polyvinyl alcohol-vinyl amine copolymer of the following structure:



wherein m and n have values of about 1 to 99 and about 99 to 1 respectively, crosslinkable at the drying surface with zirconium compounds having a valence of plus four suitable for ionic crosslinking with cellulosic paper products.

63. The creping adhesive of Claim 62 wherein the zirconium compound is selected from the group consisting of ammonium zirconium carbonate, zirconium acetylacetonate, zirconium acetate, zirconium carbonate, zirconium sulfate, zirconium phosphate, potassium zirconium carbonate, zirconium sodium phosphate and sodium zirconium tartrate.

64. The creping adhesive of Claim 62 wherein the zirconium compound is ammonium zirconium carbonate.

65. A method of creping a fibrous web that comprises providing to the interface of a fibrous web and a Yankee dryer a crosslinked creping adhesive comprising:

- a) an adhesive composition comprising organic polymers having in the polymer backbone amine groups selected from the group consisting of primary and secondary amines or mixtures of primary and secondary amines and a dialdehyde or zirconium crosslinking agent having a valence of plus four that can be crosslinked with cellulosic paper products, wherein the crosslinking agent is added directly on the Yankee ^{surface} with the copolymer without prior mixing with the copolymer, or the crosslinking agent is added to the copolymer just prior to spraying without reacting the crosslinking agent with the copolymer,
- with*
2 way

b) in an amount sufficient to promote improvement in adhesion, removing said fibrous web from said Yankee dryer by creping it off with a creping blade.

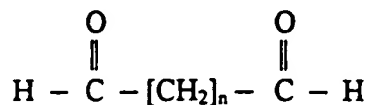
66. The method of creping a fibrous web of Claim 65 wherein the organic polymer having primary and secondary amine groups is selected from the group consisting of chitosin, polyvinylamine, polyvinyl alcohol-vinyl amine and polyaminoamide.

67. The method of Claim 65 or Claim 66 wherein the zirconium compound is selected from the group consisting of ammonium zirconium carbonate, zirconium acetylacetonate, zirconium acetate, zirconium carbonate, zirconium sulfate, zirconium phosphate, potassium zirconium carbonate, zirconium sodium phosphate and sodium zirconium tartrate.

68. The method of Claim 65 or Claim 66 wherein the zirconium compound is ammonium zirconium carbonate.

69. The method of Claim 65 or Claim 66 wherein about 0.1 to about 0.8 pounds of the adhesive are added for each ton of cellulosic papermaking fibers in the aqueous furnish.

70. The method of Claim 65 or Claim 66 wherein the dialdehyde has the following structure:



wherein n is an integer having a value of 0 to 3.

71. The method of Claim 65 or Claim 66 wherein the dialdehyde is glyoxal.

72. The method of Claim 65 or Claim 66 wherein about 0.1 to about 10 pounds of cationic softener/debinder are added for each ton of the cellulosic papermaking fibers in the aqueous furnish.

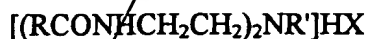
73. The method of Claim 72 wherein a nitrogenous softener/debonder is selected from the group consisting of imidazolines, amido amine salts, linear amido amines, tetravalent ammonium salts, and mixtures thereof.

74. The method of Claim 73 wherein the salt has the following structure:



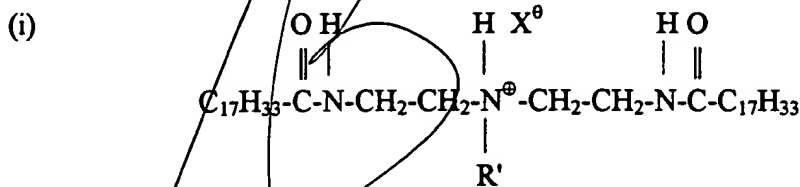
wherein EDA is a diethylenetriamine residue, R is the residue of a fatty acid having from 12 to 22 carbon atoms, and X is an anion.

75. The method of Claim 74 wherein the salt has the following structure:

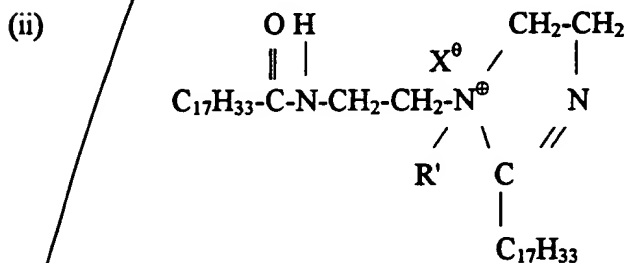


wherein R is the residue of a fatty acid having from 12 to 22 carbon atoms, R' is a lower alkyl group, and X is an anion.

76. The method of Claim 73 wherein the softener/debonder is a mixture of linear amido amines and imidazolines of the following structure:



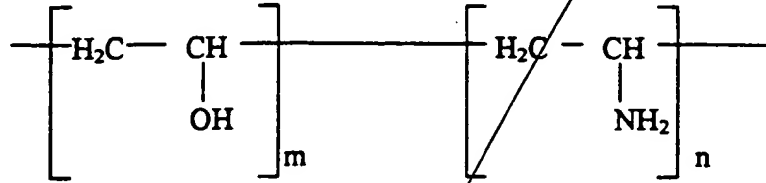
and



wherein X is an anion.

77. A method of creping a fibrous web that comprises providing to the interface of a fibrous web and Yankee dryer crosslinked creping adhesive comprising:

- a) an adhesive composition comprising polyvinyl alcohol-vinyl amine copolymer of the following structure:



wherein m and n have values of about 1 to 99 and about 99 to 1 respectively, and a dialdehyde or a zirconium compound having a valence of plus four that can be crosslinked with cellulosic paper products, wherein the crosslinking agent is added directly on the Yankee with the copolymer without prior mixing with the copolymer, or the crosslinking agent is added to the copolymer just prior to spraying without reacting the crosslinking agent with the copolymer,

- b) in an amount sufficient to promote improvement in adhesion, removing said fibrous web from said Yankee dryer by creping it off with a creping blade.

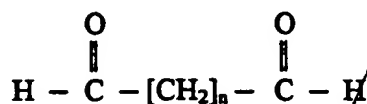
78. The method of Claim 66 or Claim 77 wherein a towel is recovered.

79. The method of Claim 77 wherein the zirconium compound is selected from the group consisting of ammonium zirconium carbonate, zirconium acetylacetonate, zirconium acetate, zirconium carbonate, zirconium sulfate, zirconium phosphate, potassium zirconium carbonate, zirconium sodium phosphate and sodium zirconium tartrate.

80. The method of Claim 77 wherein the zirconium compound is ammonium zirconium carbonate.

81. The method of Claim 77 wherein about 0.1 to about 0.8 pounds of the adhesive are added for each ton of cellulosic papermaking fibers in the aqueous furnish.

82. The method of Claim 77 wherein the dialdehyde has the following structure:



wherein n is an integer having a value of 0 to 3.

83. The method of Claim 77 wherein the dialdehyde is glyoxal.

84. The method of Claim 77 wherein about 0.1 to about 10 pounds of cationic softener/debinder are added for each ton of the cellulosic papermaking fibers in the aqueous furnish.

85. The method of Claim 84 wherein a nitrogenous softener/debinder is selected from the group consisting of imidazolines, amido amine salts, linear amido amines, tetravalent ammonium salts, and mixtures thereof.

86. The method of Claim 85 wherein the salt has the following structure:



wherein EDA is a diethylenetriamine residue, R is the residue of a fatty acid having from 12 to 22 carbon atoms, and X is an anion.

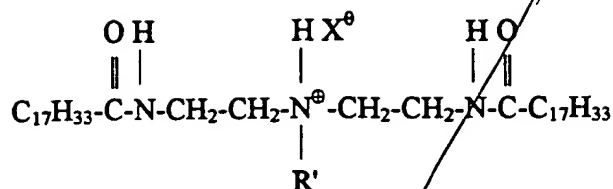
87. The method of Claim 86 wherein the salt has the following structure:



wherein R is the residue of a fatty acid having from 12 to 22 carbon atoms, R' is a lower alkyl group, and X is an anion.

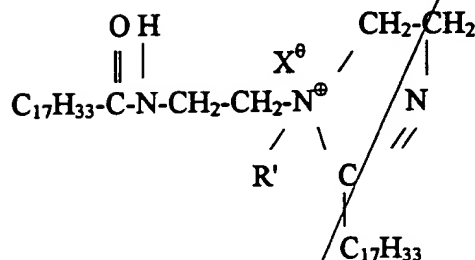
88. The method of Claim 85 wherein the softener/debinder is a mixture of linear amido amines and imidazolines of the following structure:

(i)



and

(ii)



wherein X is an anion.

89. A method of creping a fibrous web to recover a tissue that comprises providing to the interface of a fibrous web and a Yankee dryer a crosslinked creping adhesive comprising:

- a) an adhesive composition comprising organic polymers having in the polymer backbone amine groups selected from the group consisting of primary and secondary amines or mixtures of primary and secondary amines and a dialdehyde or zirconium crosslinking agent having a valence of plus four that can be crosslinked with cellulosic paper products, wherein the crosslinking agent is added directly on the Yankee with the copolymer without prior mixing with the copolymer, or the crosslinking agent is added to the copolymer just prior to spraying without reacting the crosslinking agent with the copolymer,
- b) in an amount sufficient to promote improvement in adhesion, removing said fibrous web from said Yankee dryer by creping it off with a creping blade.

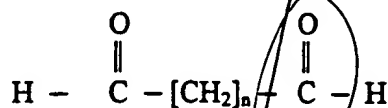
90. The method of creping a fibrous web to produce a tissue of Claim 89 wherein the organic polymer having primary and secondary amine groups is selected from the group consisting of chitosan, polyvinylamine, polyvinyl alcohol-vinyl amine and polyaminoamide.

91. The method of Claim 89 or Claim 90 wherein the zirconium compound is selected from the group consisting of ammonium zirconium carbonate, zirconium acetylacetonate, zirconium acetate, zirconium carbonate, zirconium sulfate, zirconium phosphate, potassium zirconium carbonate, zirconium sodium phosphate and sodium zirconium tartrate.

92. The method of Claim 89 or Claim 90 wherein the zirconium compound is ammonium zirconium carbonate.

93. The method of Claim 89 or Claim 90 wherein about 0.1 to about 0.8 pounds of the adhesive are added for each ton of cellulosic papermaking fibers in the aqueous furnish.

94. The method of Claim 89 or Claim 90 wherein the dialdehyde has the following structure:



wherein n is an integer having a value of 0 to 3.

95. The method of Claim 89 or Claim 90 wherein the dialdehyde is glyoxal.

96. The method of Claim 89 or Claim 90 wherein about 0.1 to about 10 pounds of cationic softener/debonder are added for each ton of the cellulosic papermaking fibers in the aqueous furnish.

97. The method of Claim 96 wherein a nitrogenous softener/debonder is selected from the group consisting of imidazolines, amido amine salts, linear amido amines, tetravalent ammonium salts, and mixtures thereof.

98. The method of Claim 97 wherein the salt has the following structure:



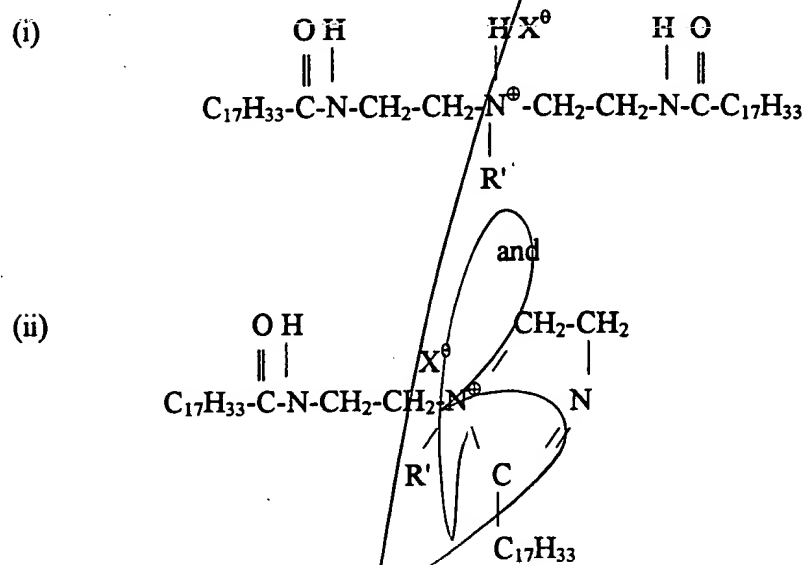
wherein EDA is a diethylenetriamine residue, R is the residue of a fatty acid having from 12 to 22 carbon atoms, and X is an anion.

99. The method of Claim 98 wherein the salt has the following structure:



wherein R is the residue of a fatty acid having from 12 to 22 carbon atoms, R' is a lower alkyl group, and X is an anion.

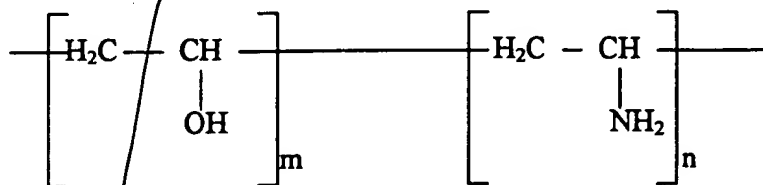
100. The method of Claim 97 wherein the softener/debonder is a mixture of linear amido amines and imidazolines of the following structure:



wherein X is an anion.

101. A method of creping fibrous web to recover a tissue that comprises providing to the interface of a fibrous web and Yankee dryer crosslinked creping adhesive comprising:

a) an adhesive composition comprising polyvinyl alcohol-vinyl amine copolymer of the following structure:



wherein m and n have values of about 1 to 99 and about 99 to 1 respectively, and a dialdehyde or a zirconium compound having a valence of plus four that can be crosslinked with cellulosic paper products, wherein the crosslinking agent is added directly on the Yankee with the copolymer without prior mixing with the copolymer, or the crosslinking agent is added to the copolymer just prior to spraying without reacting the crosslinking agent with the copolymer,

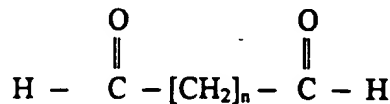
b) in an amount sufficient to promote improvement in adhesion, removing said fibrous web from said Yankee dryer by creping it off with a creping blade.

102. The method of Claim 101 wherein the zirconium compound is selected from the group consisting of ammonium zirconium carbonate, zirconium acetylacetonate, zirconium acetate, zirconium carbonate, zirconium sulfate, zirconium phosphate, potassium zirconium carbonate, zirconium sodium phosphate and sodium zirconium tartrate.

103. The method of Claim 101 wherein the zirconium compound is ammonium zirconium carbonate.

104. The method of Claim 101 wherein about 0.1 to about 0.8 pounds of the adhesive are added for each ton of cellulosic papermaking fibers in the aqueous furnish.

105. The method of Claim 101 wherein the dialdehyde has the following structure:



wherein n is an integer having a value of 0 to 3.

106. The method of Claim 101 wherein the dialdehyde is glyoxal.

107. The method of Claim 101 wherein about 0.1 to about 10 pounds of cationic softener/debinder are added for each ton of the cellulosic papermaking fibers in the aqueous furnish.

108. The method of Claim 107 wherein a nitrogenous softener/debonder is selected from the group consisting of imidazolines, amido amine salts, linear amido amines, tetravalent ammonium salts, and mixtures thereof.

109. The method of Claim 108 wherein the salt has the following structure:



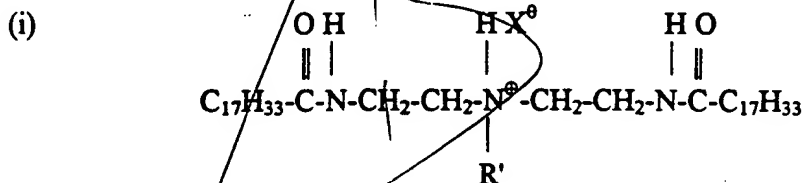
wherein EDA is a diethylenetriamine residue, R is the residue of a fatty acid having from 12 to 22 carbon atoms, and X is an anion.

110. The method of Claim 109 wherein the salt has the following structure:

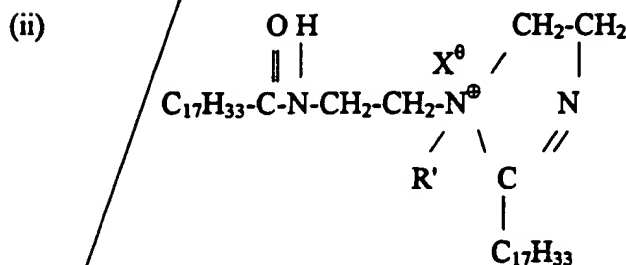


wherein R is the residue of a fatty acid having from 12 to 22 carbon atoms, R' is a lower alkyl group, and X is an anion.

111. The method of Claim 108 wherein the softener/debonder is a mixture of linear amido amines and imidazolines of the following structure:



and



wherein X is an anion.

add
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